

#### ABSTRACT

Field and laboratory experiments were conducted to develop and test methods for determining **washoff** of foliar applied herbicides typically used in forestry in the South.

Preliminary results show good agreement between results of laboratory methods used and observations from field experiments on actual precipitation events. Methods included application of known amounts of herbicide to individual leaves both in the field and in the laboratory. **Washoff** was determined by analysis of water runoff collected from individual leaves in the field following actual precipitation events, and from similarly collected water runoff from simulated precipitation events in the laboratory. Laboratory and field determinations of percent **washoff** of applied herbicide are in good agreement. As few as 10 drops of precipitation impacting a single leaf can **wash as** much 30% of applied herbicide off, and 3 mm of precipitation can wash as much as 100% of applied herbicide off foliage depending on elapsed time following application.

#### INTRODUCTION

Herbicides are a very important tool in southern silviculture. Used for weed management, they offer the land manager options for general as well as individual plant competition control. As a general tool they are typically applied by broadcast methods in which the aim is to get an even distribution across the entire site being managed. As a specific tool, herbicides are often applied to individual plants to control their unwanted growth or presence. Individual stem control is typically achieved by injection of the herbicide directly into the unwanted stem, by placement of herbicide directly at the base of the unwanted plant, or by spray of the herbicide onto the lower portion of the stem (**basal** spray). A continuing question in this age of greatly enhanced awareness of potential pesticide impacts on the environment is whether or how herbicides move from the site of application. **Washoff** from foliage is an important consideration for those modeling fate and distribution of herbicides applied in the environment as general weed control tools.

**Washoff** studies have been conducted on agricultural chemicals, but little is known about forest chemical **washoff**. Martin et al. (1) studied surface-applied, preemergence herbicide

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(cynazine, atrazine, alachlor, and propachlor) washoff from corn residue beginning 12 hours after application. Results showed herbicide through-put at application was minor. Concentrations and amounts washed off were greatest with the first 0.5 cm of simulated rain, but decreased rapidly with additional rain up to the maximum applied (3.5 cm). Washoff concentrations were not correlated with solubility. Most of the applied herbicide washed off except with cynazine. Up to 25% of applied cynazine was retained.

Baker and Shiers (2) studied the effects of herbicide (cynazine, alachlor, and propachlor) formulation and method of application on washoff from corn residue 22 hours after application. They found cynazine washed off faster than alachlor or propachlor, but that neither method of application nor formulation affected washoff. Most washoff occurred with the first 1.5 cm of simulated rain (the smallest increment applied), but 87, 69, and 88% washoff was observed with 6.8 cm of simulated rain for cynazine, alachlor, and propachlor respectively.

Insecticides have been studied in agricultural crops. McDowell et al. (3, 4, 5) and Willis et al. (6) showed that pesticide (carbaryl, fenvalerate, methyl parathion, permethrin, and toxaphene) washoff from cotton was more closely related to rainfall amount than intensity. McDowell et al. (4) also demonstrated a linear relationship between washoff and time after application with amount available for washoff decreasing by 25-40% within the first 6 hours after application.

This study composed of a set of preliminary experiments will determine the relative degree of washoff of forest herbicides from foliage as a function of time after application, amount of simulated rain, and species; and develop methods which can be enlarged upon for future studies. Typical application rates for the herbicides used is 2.24 kg ai ha . When aerially applied the herbicides are usually mixed in enough water to provide approximately 28 liters of mix per hectare. The herbicides to be tested in this study are representative of herbicides which are typically applied for their soil activity (Velpar L, hexazinone), foliar activity (Garlon 4, triclopyr) and both foliar and soil activity (Arsenal, imazapyr). All are registered forestry herbicides typically applied aerially for site preparation. Velpar L and Arsenal also are applied for pine release, but at rates lower than applied for site preparation.

#### METHODS

The herbicides were applied in late summer and early fall of 1991 to foliage excised and brought into the lab and to foliage in the field. Laboratory experiments were designed to 1) determine the maximum amount of herbicide that could be washed off foliage, and 2) determine the amount of herbicide washed off with very small amounts of simulated rain. Field studies determined washoff from foliage during actual storm events.

## Laboratory Experiments

Experiment 1. This experiment determined the maximum amount available for **washoff**, with time, after application to dogwood, Cornus florida L., sweetgum, Liquidambar styraciflua L., black cherry, Prunus serotina Ehrhart, and water oak, Quercus niara L., foliage. Stems with foliage were collected, placed in water, and transported to the laboratory where an additional section of stem was excised under water to remove embolized xylem and restore xylem function. Stems were then grouped and placed in 250 ml flasks of water. Treatment of individual leaves consisted of the addition of 10 microliters in 5-6 drops of either Arsenal, Velpar L, or Garlon 4 mixed with water. The water/herbicide mixture was prepared using distilled water and commercially available product in a ratio that simulated the mixture used in aerial applications to apply 2.24 kg ai ha<sup>-1</sup> in 28 liters of water. The herbicides were then allowed to dry for 1, 3, 6, 24 or 48 hours prior to **washoff**.

Maximum amounts that could be washed off were determined by placing treated leaves individually in 250 ml flasks, and washing each with three successive 50 ml volumes of distilled water. Flasks were shaken vigorously for 15 seconds and wash water decanted for each wash. The three volumes were combined for each leaf, and brought to a total volume of 200 ml for analysis by HPLC.

Experiment 2. This experiment determined the amount of herbicide which could be washed off treated foliage (3 replicates) with various amounts of simulated rain one hour after herbicide application. Arsenal was applied to **sweetgum**, **honeysuckle**, Lonicera sps., and blackberry, Rubus cuneifolius Pursh, foliage while Velpar L was applied to dogwood foliage as in Study 1 above. Simulated rain was applied in amounts ranging from 3 to 51 mm total. Rainfall was simulated by dropping appropriate amounts of water from a disposable syringe onto the treated leaf and collecting any water which dripped from the leaf in an erlenmeyer flask. **Washoff** collected in the flasks was diluted to 200 ml and analyzed by HPLC. Appropriate amounts of water needed to simulate the various levels of simulated rain were calculated from leaf surface area measurements.

In a similar experiment, **washoff** of Arsenal and Garlon 4 from **sweetgum** leaves was determined with 0.75 to 3.5 mm of simulated rain 48 hours after herbicide application.

## Field Experiments

Experiment 3. Field experiments were established in a cutover field in back of the George W. Andrews Forestry Sciences Laboratory. The site was instrumented with a recording and a standard rain gage. Weather forecasts and radar were obtained in the laboratory via modem connection to the Auburn Weather Information Services (AWIS) were used to determine when, in

advance of impending frontal storm events, to apply the herbicide treatments to pre-selected foliage. Foliage selected for treatment was fitted with a plastic bag, the top of which was spread with a wire ring to form a 15 cm diameter circle. This washoff trap was tied to the stem bearing the treated foliage, and suspended so that the plane of the open trap was horizontal. Foliage was selected on dogwood and sweetgum stems with three or more leaves on a stem. Herbicide was applied as in previous studies to each of three leaves with each leaf receiving five to six drops placed randomly. The herbicides were placed on the leaves three hours and in some cases 5 days before rainfall.

Experiment 4. This experiment was set up as in Experiment 3, except that only sweetgum was used, and rainfall was expected within 24 hours of treatment.

### Chemical Analysis

Chemical analysis for herbicide washoff was performed by High Performance Liquid Chromatography (HPLC). Each fraction of washoff was diluted to a known volume and analyzed by direct injection into an HPLC system composed of a Waters Associates chromatography pump Model 6000A with an Altex Ultrasphere-ODS 5 micron C-18 column, 4.6 mm X 15 cm, (5UE3280N), a Rheodyne injector Model 7125 with a 10 microliter injector loop, a SpectroMonitor III variable W absorbance detector from Laboratory Data Control, and a Spectra-Physics SP4270 computing integrator:

The mobile phase for Velpar L was acetonitrile/water (27:73, (v/v)) pumped at a flow rate of 1 ml min<sup>-1</sup> and monitored at 245.5 nm. The Arsenal mobile phase was acetic acid/water/acetonitrile (4:90:10 v/v) pumped at a flow rate of 1.5 ml min<sup>-1</sup> and monitored at 240 nm. Garlon 4 was analyzed with a mobile phase composed of acetic acid/water, acetonitrile (4:38:58 v/v) pumped at a flow rate of 1 ml min<sup>-1</sup> and monitored at 280 nm.

Analytical standards were prepared from formulated product with serial dilutions so that a comparison of amount washed off was compared with the amount applied, and all results reported as portion of applied.

### Data Analysis

All replicates were averaged and standard deviations calculated. Data for herbicide washoff are reported as the average percent of applied and standard deviation (SD). No other statistical analysis was applied.

## RESULTS AND DISCUSSION

## Laboratory Experiments

Herbicide washoff from treated foliage in this group of preliminary experiments was highly variable (Tables 1-3). Attempts to determine the maximum portion of applied herbicide which could be washed off at various times after application show some species and chemical differences. Garlon 4 and Arsenal were less readily washed from foliage than Velpar L. Generally, water oak yielded less Arsenal in washoff experiments than sweetgum, dogwood, or black cherry. Chemical and species differences are to be expected since the three chemicals tested vary in their mode of action and most effective routes of plant entry. Of the three tested, only Garlon 4 shows little soil activity, and must be principally absorbed through the leaves. Less Garlon 4 could be washed from sweetgum foliage than the other chemicals at all times tested. All three chemicals vary in the species which they affect, so different species may absorb any of the chemicals at different rates.

Simulated rain experiments (Tables 2-3) produced results similar to those found in pesticide washoff studies with agricultural chemicals on corn and cotton. One hour after application, a 6 mm rain event washed off as much herbicide as a 13 to 51 mm rain event within a species for both Arsenal and Velpar L, but species differences are apparent in this experiment with blackberry yielding less Arsenal in washoff than sweetgum, honeysuckle, or dogwood.

Reducing the amount of simulated rain and applying it 48 hours after herbicide treatment resulted in approximately 38% washoff of Arsenal from sweetgum. When compared with similar data in Table 2, a time factor is identified for Arsenal which was not apparent in the first washoff studies. In addition, the 38 % washoff with a 3.5 mm precipitation event at 48 hours is approximately half the maximum that could be washed off 24 hours after application. Studies with Garlon 4 show a similar trend. A trace of precipitation (.75-3.5 mm) occurring 48 hours after application washed off approximately half the maximum amount of Garlon 4 that could be washed from sweetgum (Table 1).

These preliminary studies indicate that there are species, chemical, and time considerations in herbicide washoff from treated foliage. In general, however, the data correlate well with the data published for other agricultural pesticides on row crop residues. Velpar L and Arsenal are more readily washed from foliage than Garlon 4 for the species tested. Also, the majority of herbicide that is washed from treated foliage comes off with the first few drops of precipitation which impact treated leaves.

## Field Experiments

The field setup for the first storm event was conducted without benefit of current radar and weather information, and the storm which looked imminent did not appear. Four sets of **sweetgum** foliage treatments were established one each at 2 hour intervals in anticipation of this storm which did not occur until 5 days later. Therefore, all treatments were combined as replicates for the intermediate time between establishment and rain (124 hours). Just prior to the storm which subsequently materialized (72 mm) 4 more sets of treatments were established on **sweetgum** and 4 on dogwood. Because they were so similar in residue content, they too were combined as replicates for an intermediate time prior to application of 3 hours. Velpar L was more completely washed from **sweetgum** and dogwood foliage 3 hours after treatment than Arsenal (Table 4). **Washoff** of Velpar L from foliage treated 124 hours prior to the storm was much greater for dogwood foliage than for **sweetgum** indicating a species difference which increases with time.

A second storm event was studied which came in two parts. Precipitation was sudden, but light, and occurred 24 hours (1 mm) and 48 hours (2 mm) after application for a total of 3 mm precipitation. Only **sweetgum** foliage was studied in this test with 5 replications. The results were highly variable, but no differences were observed in total **washoff** of Velpar L and Arsenal in this experiment (Table 5). The total portion of Arsenal washed off **sweetgum** foliage in this actual rain event is very similar to that observed in laboratory experiments with 3.5 mm of simulated rain applied 48 hours after treatment (Table 3). Velpar L was not studied in that experiment. Velpar L **washoff** in this experiment (Table 5) appears to be strongly correlated with amount of precipitation.

## SUMMARY

The results reported here agree well with reports from agricultural systems working principally with insecticides, but demonstrate the added complexity encountered in forest ecosystems. Herbicide **washoff** is a function of chemical, species, and time interactions which are themselves probably affected by many other factors including leaf age, surface integrity, leaf morphology (sun **vs** shade leaves), disease, etc. Some generalizations useful to modelers' may be made with additional experiments which should focus on chemical, species, time, rain volume interactions. Rain volume studies should focus on the small precipitation events. Time considerations should focus on short term (1-3 hours) for identification of some species differences in terms of surface adsorption, and on long term (>48 hours) for identification of species differences in foliar absorption.

## LITERATURE CITED

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## TABLES

Table 1. Maximum amounts of herbicide washed from foliage at distinct time intervals after application.

HERBICIDE/SPECIES	HOURS AFTER APPLICATION				
	1	3	6	24	48
PERCENT OF APPLIED (SD)					
VELPAR L					
Sweetgum	95(1.4)	95(1.1)	94(1.7)	-	
Water Oak	93(0.7)	100(2.2)	91(1.4)	96(6.2)	
99(1.2)					
Dogwood	83(14.4)	100(14.4)	94(0.2)	-	
Black Cherry	89(2.0)	90(1.4)	90(1.0)	77(19.2)	
80(29.0)					
ARSENAL					
Sweetgum	84(13.7)	72(13.9)	88(10.0)	73(4.8)	-
Water Oak	63(17.6)	61(24.5)	51(7.8)	61(30.2)	-
Dogwood	97(1.9)	90(9.8)	87(12.4)	83(0.2)	-
Black Cherry	92(2.8)	72(6.7)	80(8.5)	66(3.7)	-
GARLON 4					
Sweetgum	62(3.0)	-			
21(6.5)					

Table 2. Herbicide washed off foliage with different amounts of simulated rain applied 1 hour after herbicide treatment.

RAIN (MM)	ARSENAL				VELPAR L
	SWEETGUM	HONEYSUCKLE	BLACKBERRY	DOGWOOD	DOGWOOD
	PERCENT OF APPLIED(SD)				
3	100(7.2)	100(3.6)	41(2.8)	-	
6	100(11.3)	100(6.0)	48(9.1)	90(2.8)	91(1.7)
8	96(8.3)	100(4.3)	61(8.3)	-	
10	99(10.8)	100(1.0)	57(3.0)	-	
13	98(8.8)	83(15.7)	59(1.3)	86(15.8)	86(3.5)
25	-			99(1.1)	92(1.6)
38	-			92(13.3)	89(1.6)
51	-			82 (25.9)	92(2.1)

Table 3. Herbicide washed off **sweetgum** foliage with different amounts of simulated rain applied 48 hours after herbicide treatment.

RAIN (MM)	ARSENAL	GARLON 4
	PERCENT OF APPLIED(SD)	
0.75	38(13)	11(2.8)
1.75	38(12)	12(1.1)
3.50	37(15)	17(3.8)

Table 4. Portion of applied herbicide washed from treated foliage during a 74 mm precipitation event.

HERBICIDE	SPECIES	TIME AFTER TREATMENT	
		3 HOURS	124 HOURS
		PERCENT(SD)	
VELPAR L	SWEETGUM	63(31.9)	28(6.3)
	DOGWOOD	72(8.3)	62(3.9)
ARSENAL	SWEETGUM	39(15.0)	
	DOGWOOD	45(16.3)	

Table 5. Portion of applied herbicide washed from **sweetgum** during a 3 mm rain event 24 hours and 48 hours after treatment.

HERBICIDE	TIME AFTER TREATMENT(MM OF PRECIPITATION)		
	24 HOURS(1 MM)	48 HOURS(2 MM)	48 HOURS(TOTAL)
	PERCENT(SD)		
VELPAR L	10(15)	29(3)	39(14)
ARSENAL	20(9)	22(9)	42(16)